

# EFFECT OF CHEMICAL TREATMENTS ON BENEFICIATION OF LOW RANK COALS

M. Polat\*, S. Chander\* and D. C. Cronauer\*\*

\* Mineral Processing Section  
Penn State University  
University Park, PA 16802

\*\* Amoco Oil Company  
Research and Development Department  
PO Box 3011  
Naperville, IL 60566

Keywords: Lignite, flotation, sulfurous acid treatment

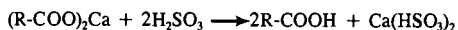
## ABSTRACT

Cleaning of low rank coals is desirable for preparation of feed stock for liquefaction of coal. In this investigation, the effect of chemical pretreatment on the beneficiation of low rank coals was studied. In the first phase of the research, a lignite sample from Texas with an ash content of 12.9% was pretreated with sulfurous acid prior to separation. Treated coal was subjected to flotation or Liquid-Liquid Extraction (LLE) for further cleaning. A final clean coal product of 4.4% ash was obtained with a combustible matter recovery of about 95%. In the second phase, a chemically treated low rank coal sample with 3.3% ash was further cleaned using a mild agglomeration stage prior to flotation. When a non-ionic, block co-polymer surfactant was used with the oily collector, a clean coal product of 1.85% ash could be obtained with a combustible matter recovery of over 85%.

## INTRODUCTION

It is well known that lignites are very difficult to clean from the mineral matter using conventional flotation due to their poor floatability. According to Sun (1954) the floatability index of lignites was 12 taking Ceylon Graphite with an index of 100 as standard. The average floatability index for hvA bituminous coals was 94 on the same scale. The poor floatability was also confirmed by Aplan (1976, 1980 and 1988) who observed that the measured contact angle using captive bubble method was zero for lignites. Use of an oily collector alone does not improve the floatability due to low adsorption of oil on lignites (Sun, 1954; Gayle et al, 1965). This is most probably due to high oxygen content of lignites and the abundance of surface functional groups (Fuerstenau et al, 1983; Gutierrez-Rodriguez and Aplan, 1984 and Schobert, 1990). It was reported that the average oxygen content of lignites could be as high as 30%, carboxylic groups constituting about half this amount (Quast and Readett, 1987). Another important consequence of the presence of the surface functional groups is that these groups act as ion exchange sites for cations such as Na, Ca, Mg and K, and may result in the accumulation of carbonaceous ash. In general 90 - 100% of the Na, 75 - 90% of the Mg, 50 - 75% of the Ca and 35 - 50% of the K in low rank coals may be accumulated by the ion exchange process (Schobert, 1990). These cations which are bonded to the organic portion of the coal as inherent ash are practically impossible to clean using conventional separation techniques.

Chemical treatment of lignites prior to separation may be beneficial due to dissolution of these ion exchange cations, resulting a direct decrease in the ash content. Different types of pretreatment have been suggested in the literature. Mochida et al showed that pretreatment of lignites using HCl improved their conversion during coal liquefaction (1983). Cronauer et al utilized sulfurous acid to chemically clean the lignites (1991). The authors suggested that sulphurous acid converts carboxylic salts to free carboxylic acids through the following reaction:



It was pointed out that sulfurous acid was cheap, less corrosive and easily recoverable. In addition to dissolving the cations from the coals structure, the dissolution process may change the floatability of lignite due to its effect on the surface functional groups.

Objective of this study was to investigate deep cleaning of lignites using a combination of chemical dissolution and physico-chemical separation methods. The study was conducted in two parts. In the first part a raw lignite sample was subjected to chemical treatment using sulfurous acid under a variety of conditions. The treated sample was then further cleaned using Liquid-Liquid Extraction (LLE) method using heptane as the carrier liquid. In the second part a pretreated lignite sample was subjected to cleaning using flotation or mild oil agglomeration followed by flotation, MOAF. A block co-polymer surfactant was also used in this part of the study to improve ash rejection.

## EXPERIMENTAL

### Material

The raw lignite sample used in the first part of the study was obtained from Amoco Company, Naperville, IL and originated from Martin Lake, Texas. The sample had an ash content of 12.9% and was less than 6.35 mm in particle size. A semi-quantitative spectroscopic analysis on the ashed lignite showed that the ash material contained about 10% Ca, 5% Mg and 1% Na. The Si content was around 2%. The sample was ground to a feed size of -150  $\mu\text{m}$  to be used in the flotation and LLE studies.

The coal sample used in second part of the study had been pretreated by the Amoco Oil Company with sulfurous acid and had an ash content of about 3.3%. It is referred as Sample No. 2 and had a narrow size distribution of 212x1650  $\mu\text{m}$ . It was wet ground to various feed sizes for the flotation or mild oil agglomeration-flotation studies.

A polypropylene/polyethylene block co-polymer surfactant was used to enhance the ash rejection during flotation or mild oil agglomeration-flotation studies. This surfactant was previously shown to be very selective in the flotation of a low rank coal (Chander et al, 1993). It was added to the system in an oil-dispersed form. The chemical structure of the surfactant is given in Figure 1.

### Methods

#### *Liquid-Liquid Extraction*

The process of Liquid-Liquid Extraction (LLE) involves selective transfer of hydrophobic particles of organic matter from aqueous phase to an emulsion phase. This process is especially useful at fine sizes (Hsu and Chander, 1988). The tests were conducted in a baffled, 500 ml vessel of standard geometry (Holland and Chapman, 1966). The vessel was slightly tapered at the bottom to allow for easy removal of the separated phases. The total solution volume in a given test was 400 ml. The slurry contained 1% solids by weight and 15% heptane as the organic phase. Following initial conditioning to wet and disperse the lignite, the desired reagents were added and the slurry was conditioned 10 more minutes. Heptane was added and the stirring was continued for preset periods of time at a selected stirrer speed. Finally, the emulsion phase containing the coal particles was allowed to separate out from the aqueous phase containing the mineral matter. Both phases were removed from the bottom of the vessel, filtered, dried and analyzed. Practically all the heptane was recovered from the emulsion phase during the filtering step.

#### *Flotation*

A Wemco model 21260-01 flotation machine equipped with a 1 liter cell was used in the flotation experiments. The impeller speed was kept constant at 1000 rpm in all the flotation tests. The solid concentration was kept constant at 5% when flotation was used alone. For the tests where a mild oil agglomeration step was utilized prior to flotation, the solid concentration in the flotation cell was determined by the amount of solids in the agglomeration stage. The slurry was preconditioned for 3 minutes before any reagent addition. Dodecane and methylisobutylcarbinol (MIBC) were used as the oily collector and frother, respectively. The experiments were carried out at the natural pH of the slurry which was mostly on the acidic side due to prior acid treatment. The flotation products were dried, weighed and analyzed.

#### *Mild Oil Agglomeration Flotation*

A limited number of tests were performed in which a mild agglomeration stage was combined with flotation. This process is referred to as MOAF in this article. In this procedure the conditions were chosen such that the coal particles were agglomerated in a high shear environment to produce loose agglomerates of about one millimeter in diameter. For this purpose dodecane or dodecane-block co-polymer surfactant solution was emulsified in a blender for three minutes. A coal slurry of 400 ml of varying solids content was added into this solution and the blending was continued for 3 more minutes. This procedure produced loose agglomerates of the coal particles. The slurry containing the agglomerates was transferred into the flotation cell and flotation tests were carried out by addition of frother only. In some cases, dodecane-surfactant mixture was added directly to the coal slurry prior to any blending procedure.

## RESULTS AND DISCUSSIONS

### Studies with the Raw Texas Lignite Sample

#### *Pretreatment with Sulfurous Acid*

A 6.0% aqueous solution of  $\text{SO}_2$ , sulfurous acid ( $\text{H}_2\text{SO}_3$ ), was utilized to dissolve the cations from the coal structure. The experiments were conducted at different acid concentrations and temperatures using a nominal  $-150\text{ }\mu\text{m}$  feed material. An optimum decrease in the ash content was observed at an acid concentration of 1.0% at  $50^\circ\text{C}$ . Under these conditions the ash content of the lignite sample decreased from 12.9% down to about 6.5% with a combustible matter recovery of almost 100%. A semi-quantitative spectrographic analysis conducted on the as-received and  $\text{H}_2\text{SO}_3$  treated samples showed that there was approximately a ten-fold decrease in the Ca, Mg and Na contents of the lignite sample, supporting the reverse extraction of the cations from the carboxylate structure. The fact that the Na content also decreased substantially is an important result since sodium is known to cause slagging problems in combustion.

Both the as-received and the chemically treated samples were subjected to zeta potential measurements in order to determine the effect of chemical treatment on the electrokinetic behavior. A Lazer Zee Meter from Pen Kem Inc., New York, was used for this purpose. It was observed that the point of zero charge of the as-received sample was around a pH of 2.4. This was in a good agreement with the data in the literature (Arnold and Aplan, 1989). The point of zero charge decreased with increasing concentration of  $\text{H}_2\text{SO}_3$  and found to be around a pH of 1.8 for an acid concentration of 6.0%.

In order to determine the effect of the acid treatment on the floatability of the lignite sample contact angle measurements were conducted using a method first described by Wei et al (1992). In this method a particle was gently placed at the air-water interface and the cross sectional areas of both parts of the particle above and below the interface were measured with a microscope coupled to an image analyzer. The ratio of these areas are related to the contact angle. To prepare the sample for the contact angle measurements a sufficient amount of lignite sample was screened to obtain a narrow size fraction of  $600\times 850\text{ }\mu\text{m}$ . Half of this sample was treated with distilled water whereas the other half was treated with 1.0% sulfurous acid. The samples were dried in a vacuum oven at room temperature. Measurements conducted on about 150 particles for each sample showed that the mean advancing contact angle increased from 62 degrees for the untreated coal to 72 degrees for the  $\text{H}_2\text{SO}_3$  treated coal. This apparent increase in the contact angle suggests that the sulphurous acid treatment results in an increase in the hydrophobicity of the lignite sample.

#### *Flotation*

Flotation experiments were carried out using both the untreated, 12.9% ash, and the  $\text{H}_2\text{SO}_3$  treated, 6.5% ash, samples. The feed size of the both samples was  $-150\text{ }\mu\text{m}$ . The concentration of dodecane and MIBC were 20 kg/T and 0.8 kg per ton of coal, respectively. The flotation tests were carried out at the natural pH values of 6.3 for the raw sample and 4.4 for the  $\text{H}_2\text{SO}_3$  treated sample. A quartz depressant,  $\text{Na}_2\text{SiO}_4$ , was also used in the flotation tests. It was observed that the untreated sample could not be beneficiated using flotation. The ash content of the product was 12.6% after 8 minutes of flotation with a coal recovery of 50.4 in the presence of 0.4 kg of  $\text{Na}_2\text{SiO}_4$  per ton of coal. The flotation response of the treated sample was also not very promising. The ash content of the clean coal product was about 5.5% when the coal recovery was 95%. The high coal recovery obtained in the case of the treated sample was in agreement with the observation stated in the preceding section that acid treatment should enhance the floatability of the lignite sample. Since no satisfactory results were obtained using flotation, LLE method was employed in subsequent tests.

#### *Liquid-Liquid Extraction*

In this series of tests, heptane was emulsified with lignite slurry in a standard vessel. The lignite particles were extracted in the hydrocarbon to form an emulsion phase. Upon completing the transfer of coal particles from aqueous phase into the emulsified heptane phase, the mixing was stopped and the phases were allowed to separate. The emulsion containing the coal particles was separated from the aqueous phase which contained the mineral matter. The LLE experiments were carried out under a variety of test conditions with the sulfurous acid treated lignite sample which contained 6.5%. The variables tested included pH, stirrer speed, mixing time and depressant type and concentration. The best ash rejection was obtained at the natural pH value of the sample and at a stirrer speed of 1800 rpm. The subsequent testing was carried out under these conditions. The result of the mixing time experiments are given in Table I. It can be seen that the ash content of the product does not vary appreciably whereas the combustible matter recovery steadily increases

with increasing mixing time.

Sodium silicate and sodium dicarbonate were used as depressants at different concentrations to increase the efficiency of separation. In the case of  $\text{Na}_2\text{SiO}_4$ , a clean coal product of 4.6% ash with a combustible matter recovery of 94% was obtained at a  $\text{Na}_2\text{SiO}_4$  concentration of 0.13 kg per ton of coal. The results obtained with  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  were slightly better. A clean coal product of 4.4% ash was obtained with a combustible matter recovery of 95% at a  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  concentration of 0.25 kg per ton of coal.

#### Studies with the $\text{H}_2\text{SO}_4$ Treated No. 2 Sample

The sample was processed using conventional flotation or mild oil agglomeration flotation, MOAF in order to further reduce the ash content. The quality of separation was increased in both cases when a block co-polymer surfactant was added into the oily collector. The results of these studies are given in the following paragraphs.

#### *Flotation*

The sulfurous acid treated sample was ground to a nominal feed size of  $-150 \mu\text{m}$  and floated at a natural pH of 2.9. A clean coal product of 2.2% ash was obtained with a combustible matter recovery of 70% when the concentration of the oily collector was 4.0 kg per ton of coal. The ash content did not change with an increase in the oil concentration up to 40 kg per ton of coal. However, the combustible matter recovery slightly increased to 74%. When 0.8 kg of a block co-polymer surfactant was added into 4.0 kg of oil per ton of coal, the combustible matter recovery increased to 87% and the ash content of the clean coal was 2.2%. The ash content of the pretreated coal sample could not be reduced to less than 2.0% when additional flotation studies were performed. Hence, a mild oil agglomeration stage was used prior to flotation step.

#### *Mild Oil Agglomeration Flotation*

Initial MOAF tests were carried out to determine the best particle size for ash rejection. The concentration of the oily collector and the surfactant were 250 kg and 8 kg per ton of coal, respectively. Three different feed sizes of  $-150 \mu\text{m}$ ,  $-60 \mu\text{m}$  and  $-38 \mu\text{m}$  were tested in these experiments. The results are given in Table 2. It was observed that a clean coal product of 2.0% ash could be obtained with a combustible matter recovery of 85% when the nominal feed size was  $-38 \mu\text{m}$ . Neither the ash nor the coal recovery was better for the other two feed sizes. Hence, subsequent studies were carried out using a feed size of  $-38 \mu\text{m}$ . In the next set of MOAF tests, sodium hexametaphosphate (calgon) was added into the coal slurry to promote dispersion of the coal particles. The collector and the surfactant concentrations were kept the same as before. Calgon concentrations of 0.02 kg, 0.1 kg, 0.5 kg and 2.0 kg per ton of coal were tested. The results of these tests are given in Table 3. It can be seen that addition of the dispersant improved the separation appreciably. A clean coal product of 1.94% ash could be obtained with a coal recovery of 92% when 0.5 kg of calgon per ton of coal was added. In order to determine the effect of the block co-polymer surfactant, the concentration of the surfactant was varied keeping the oil concentration constant at 250 kg per ton of coal. The amount of surfactant used was 0, 2, 8, 8 and 25 kg per ton of coal, respectively. The results are given in Table 4. It was observed that increasing the amount of the surfactant in the system decreased the ash content while increasing the combustible matter recovery. The surfactant amount of 25 kg per ton of coal resulted in a better product. In another set of experiments the oil to surfactant ratio was kept constant at 10. The oil amounts in these tests were 125, 250 and 500 kg per ton of coal. The ash contents and the combustible matter recoveries for these tests are given in Table 5.

In the above tests the emulsification of oil-surfactant solution was carried out in the presence of the coal slurry. A different set of experiments was conducted where the oil-surfactant solution was emulsified for 3 minutes prior to the addition of the coal slurry in order to reduce the amount of surfactant and oil used in the process. The coal slurry was added to this emulsified phase and the agglomeration was initiated. The experiments were carried out using the same oil to surfactant ratio of 48. The oil amounts employed in this set were 48, 96 and 192 kg per ton of coal. The results of these experiments are given in Table 6. It was seen that pre-emulsification decreased the amount of surfactant required for separation. A clean coal product of 1.85% ash could be obtained with a coal recovery of 85% using 192 kg of oily collector with 2 kg of surfactant per ton of coal.

### CONCLUSIONS

Deep cleaning of lignite samples was investigated using a combination of chemical dissolution and physico-chemical separation methods. Sulfurous acid,  $\text{H}_2\text{SO}_3$ , was utilized in the dissolution studies. The treated samples were subjected to liquid-liquid extraction, flotation and mild agglomeration-flotation separations to further decrease the ash content.

The findings of this study can be summarized as follows:

1. In the absence of sulfurous acid treatment, lignite could not be beneficiated.
2. Sulfurous acid leaching was very effective in removing salts of Ca, Mg and Na. A clean coal sample of 6.5% ash was obtained from a raw lignite sample with 12.9% ash using a 1.0% solution of sulfurous acid.
3. The acid treatment rendered the low rank coal more hydrophobic most probably due to some chemical changes at the surface during the dissolution of the cations from the carboxylate structure.
4. A clean coal product of 4.4% ash was obtained with 95% combustible matter recovery from a 12.9% ash lignite sample by a combination of sulfurous acid treatment and LLE separation.
5. For a second sample prepared by Amoco Oil Company, the ash content of sulfurous acid treated coal was reduced from 3.3% to 1.85% with a combustible matter recovery of 85%, using the mild oil agglomeration-flotation method.
6. Even though large amount of hydrocarbon was used to obtain the clean coal products of desirable quality, it was possible to recover and recycle most of it.

#### ACKNOWLEDGEMENTS

The authors acknowledge the support from the Department of Energy, under contract number DE-AC22-91PC91051.

#### REFERENCES

- Aplan, F. F. (1976), "Coal Flotation", A. M. Gaudin Memorial International Flotation Symposium, Ed. by M. C. Fuerstaneau, pp. 1235-1264.
- Aplan, F. F. (1980), "Estimating the Floatability of Western Coal", Gold, Silver, Uranium and Coal, Geology, Mining, Extraction and Environment, Ed. by M. C. Fuerstaneau and B. R. Palmer, New York, pp. 380-398.
- Aplan, F. F. (1988), "How the Nature of Coal Influences Its Cleaning", Industrial Practice of Fine Coal Cleaning, Ed. by R. R. Klimpel and P. T. Luckie, SME Littleton, CO, pp. 99-111.
- Arnold, B. J. and Aplan, F. F. (1989), "The Hydrophobicity of Coal Macerals", Fuel, Vol. 68, pp. 651-658.
- Chander, S., Polat, H. and Mohal, B. (1993), "Flotation and Wettability of a Low Rank Coal in the Presence of Surfactants", Preprint 93-64, SME Annual Meeting in Reno, Nevada.
- Cronauer, D., Joseph, T.J., Davis, A., Glick, D. and Luckie, P.T. (1992), "The Beneficiation of Martin Lake Texas Lignite", Fuel, Vol. 71, pp. 65-73.
- Fuerstaneau, D. W., Rosenbaum, J. M. and Laskowski, J. (1983), "Effect of Surface Functional Groups in the Floatability of Coal", Colloids and Surfaces, Vol. 8, pp. 153-174.
- Gayle, J. B., Eddy, W. H. and Shotts, R. O. (1965), "Laboratory Investigation of the Effect of Oxidation on Coal Flotation", Report of Investigations 6620, US Bureau of Mines.
- Gutierrez-Rodriguez, J. A. and Aplan, F. F. (1984), "The Effect Oxygen on the Hydrophobicity and Floatability of Coal", Colloids and Surfaces, Vol. 12, pp. 27-51.
- Holland, F. A. and Chapman, F. S. (1966), Liquid Mixing and Processing in Stirred Tanks, Reinhold Publishing, New York.
- Hsu, T. C. and Chander, S. (1988), "Interfacial and Colloidal Effects in Liquid-Liquid Separation of Ultrafine Coal", Interfacial Phenomena in Biotechnology and Materials Processing, Ed. by Y. A. Attia, B. M. Moudgil and S. Chander, Elsevier Science Publishers B. V., Amsterdam, pp. 399-411.

Mochida, I., Moriguchi, Y. and Shimomara, T. (1983), Fuel, Vol. 62, p. 471.

Quast, K. B. and Readett, D. J. (1987), "The Surface Chemistry of Low Rank Coals", Advances in Colloid and Interface Science, Vol. 27, pp. 169-187.

Schobert, H. H. (1990), The Chemistry of Hydrocarbon Fuels, Butterworths, Boston.

Sun, S. C. (1954), "Hypothesis for Different Floatabilities of Coals, Carbons and Hydrocarbon Minerals", Transactions of AIME, Vol. 199, PP. 67-75.

Wei, D., Chander, S. and Hogg, R. (1992), "Distribution of Wettability of Coal", Coal Preparation, Vol. 10, pp. 37-45.

Woodburn, E. T., Robbins, D. J. and Flynn, S. A. (1983), "The Demineralization of a Weathered Coal by Froth Flotation", Powder Technology, Vol. 35, pp. 1-15.

Table 1. Results of the LLE tests as a function of mixing time.

Mixing Time (minutes)	Ash (%)	CMR (%)
5	4.63	93
10	4.80	95
20	4.69	96
40	4.90	97
80	4.78	98

Table 2. Results of the MOAF tests as a function of feed size.

Feed size	Ash (%)	CMR (%)
-150 $\mu$ m	2.40	69
-60 $\mu$ m	2.40	63
-38 $\mu$ m	2.02	85

Table 3. Results of the MOAF tests as a function of calgon concentration.

Concentration	Ash (%)	CMR (%)
0.00 kg/T	2.02	85
0.02 kg/T	1.97	93
0.10 kg/T	2.03	88
0.5 kg/T	1.94	92
2.0 kg/T	1.97	92

Table 4. Results of the MOAF tests as a function of surfactant concentration.

Surfactant Concentration	Ash (%)	CMR (%)
0 kg/T	2.23	82
2 kg/T	2.25	82
8 kg/T	2.02	85
25 kg/T	1.96	88

Table 5. Results of the MOAF tests as a function of collector concentration at a fixed collector to surfactant ratio of 10.

Collector Concentration	Ash (%)	CMR (%)
125 kg/T	2.49	75
250 kg/T	1.96	88
500 kg/T	1.99	91

Table 6. Results of the MOAF tests as a function of collector concentration at a fixed collector to surfactant ratio of 48\*.

Collector Concentration	Ash (%)	CMR (%)
48 kg/T	2.18	58
96 kg/T	1.95	72
192 kg/T	1.85	85

\* Reagents were Pre-emulsified in a blender before addition of coal slurry.

Figure 1. Structural formula of PPO/PEO block co-polymer used in this study

